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MOSCON CONFERENCE ON PROBLEMS OF CHEMICAL KINETICS,  
CATALYSIS, AND REACTIVITY

Vestnik Akademii Nauk SSSR, Vol 25, No 10  
Moscow, Oct 55

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The most important problems of contemporary theoretical chemistry, which are at the same time of great practical importance, are those dealing with chemical kinetics, catalysis, and reactivity. These problems were discussed at a conference of physical chemists, organic chemists, and inorganic chemists held 23-24 June 1955 at Moscow. This was the first time that problems of the theory of chemical processes were discussed at a gathering as extensive as this. The purpose of the conference was to outline the contemporary state of the theory, to bring out the basic directions of its development, to formulate questions for discussion, and to organize the collective work of chemists on the theory of chemical processes.

In connection with the conference, two books were published: an introductory report by N. M. Semenov entitled O Nekotorykh Probleмах Khimicheskoy Kinetiki i Reaktivnosti (Concerning Some Problems of Chemical Kinetics and Reactivity), 154, and a collection of reports by participants at the meeting entitled Voprosy Khimicheskoy Kinetiki, Kataliza, i Reaktivnosti (Problems of Chemical Kinetics, Catalysis, and Reactivity), 1955. The latter book contains 66 reports. More than 550 chemical scientists from 31 cities of the Soviet Union participated in the conference. More than 100 of them took part in the discussions.

The conference was opened by an introductory address given by Academician V. N. Kondratyev, chairman of the Organizational Committee. He characterized the original contents of the reports presented for discussion and summarized the concrete problems formulated in the reports. In this manner a matter-of-fact arrangement of the daily program was achieved, which contributed to the proper organization of the work of the conference.

The majority of chemical processes are of a very complex nature. The mechanism of these processes comprises many interdependent elementary interactions between particles of matter: radicals, free atoms, complexes, and ions. For that reason considerable attention was given in the reports and discussions to a consideration of elementary interactions and to their dependence on the chemical structure of the substances which participate in the reaction.

Free radicals and atoms readily react with molecules and for that reason represent a frequently encountered type of active intermediate products in complex chemical processes, particularly those involved in chain reactions. The detection and identification of particles of this type, and also the study of their reactions, form a task which is not easy by any means. Nevertheless, this task can be accomplished with the aid of modern physicochemical and physical methods of investigation (mass spectroscopy, radiospectroscopy, study of light spectra, magnetic resonance methods, tracer atom methods, etc.)

Data on the chemistry of free radicals and on the elementary reactions of free atoms and radicals were presented at the conference. Several new types of elementary reactions were considered which make it possible to understand the characteristic traits of such important processes from the practical point of view as oxidation of organic substances (particularly of hydrocarbons), polymerization, cracking, etc. Many discussions dealt with the so-called Polanyi rule. This rule relates the fundamental quantity which characterizes the reactivity of radicals, i. e., the energy of activation, to the heat effect of the elementary reaction. However, no strict theoretical proof of this rule

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could be given hitherto. This is due to some extent to the inadequate attention which has been paid to problems of quantum chemistry. Without a sufficient development of the quantum-mechanical theory of chemical structure and of elementary chemical reactions, it will hardly be possible to achieve a measurable degree of success in work on problems dealing with interrelationships between chemical kinetics and organic chemistry. The theory of the activated complex, which makes it possible to interpret the mechanism of elementary reactions, is not being subjected to adequate study. In only a few reports and discussions held at the conference were the problems of this theory touched upon. In these instances, the advisability of applying it to the solution of a number of practical questions was demonstrated (this applies particularly to the calculation of steric factors which characterize the spatial hindrance that is effective when an elementary reaction takes place).

Many important chemical reactions take place in the liquid phase and in solutions. Nevertheless, the detailed mechanism of these processes is not being investigated to an adequate extent. The inadequate extent of development of the theory of the liquid state is partly responsible for this situation. One must develop reliable methods for the detection of active substances participating in liquid-phase reactions and for the determination of their concentration and also expand work aiming at the clarification of the role of solvents forming the medium in reactions that take place in the liquid phase. When elementary interactions between ions are subjected to scrutiny, one must take into consideration the close analogy between these interactions and the elementary processes of electrochemical transformations (e. g., the transfer of electrons by the tunnel effect).

Great attention was paid at the conference to a consideration of the problem in regard to the role played by complexes in the course of chemical processes. It is known that the properties of many molecules change considerably after they have entered into the composition of complexes. This circumstance is reflected in the kinetics of processes involved in the formation of complexes. Apparently, an important part can be played in a number of cases by complexes in which the transition of an oxygen atom into a positively ionized trivalent state takes place. This applies, for instance, to the very reactive complexes of magnesium phthalocyanine with a number of molecules. In studying the reactivity of such compounds, one must distinguish between electrically charged complexes and neutral complexes.

As has been pointed out at the conference, one must expand work on the determination of the quantitative characteristics of elementary processes in addition to expanding research on these processes in general. One must also increase the volume of experimental work on elementary processes (elementary reactions), because the difficulties which are inherent in their study often have the result that experimental work is replaced to a greater extent than justified by the consideration of hypothetical and abstract schemes.

The investigation of elementary processes and of the mechanism of chemical reactions requires considerable improvements in the equipment of laboratories. One must subject these processes to many-sided investigation, using for this purpose the whole armamentarium of physical, physicochemical, and chemical methods.

General attention was attracted at the conference by the interpretation of the concept "reaction mechanism." The question was asked as to whether one should regard as the reaction mechanism the sum total of all elementary stages together with their complete quantitative characterization or designate as mechanism the order in which products are formed in complex reactions and the succession of microscopic stages. As an objection against the first definition

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of mechanism, the consideration was advanced that there are practically no reactions in which all the processes are known (one or two exceptions to this rule exist).

Generally speaking, a broad section of chemists associates the concept of reaction mechanism with obtaining information on the ways along which the chemical transformation proceeds, this information being more or less detailed, depending on the possibilities for investigation which are open to the experimenter. In the future it will be necessary to introduce definitive clarity into the ideas underlying this concept: otherwise it will become applicable only to a limited range of investigations, which is hardly justifiable.

Much has been said at the conference in regard to the impossibility of considering the reactivity of substances as a merely qualitative characteristic. One must also give a quantitative kinetic characterization to the reactivity by assigning a velocity constant to the reactions that take place. For this purpose one should use quantum mechanics and the concepts of the electronic theory and valency theory.

During recent years the reactions of isotope exchange, particularly of hydrogen exchange, have acquired a great significance for the investigation of reactivity. For that reason it is necessary to expand investigations aimed at the clarification of the details of the hydrogen exchange mechanism in organic substances of different types.

Of considerable interest in organic chemistry are phenomena of the formation of two series of derivatives corresponding to two isomeric forms of a substance. These phenomena may be caused either by a dual reaction capacity of substances or by their tautomerism. At the present time it is still difficult to predict on the basis of theoretical considerations only when tautomeric transformations will take place and when a dual (or multiple) reaction capacity will be exhibited. For that reason it is also necessary to expand experimental research along these lines.

The organic chemists who participated in the work of the conference pointed out that the method of organic synthesis by itself is of great importance for solving problems which pertain to reactivity and to methods of controlling organic synthetic reactions. One of the most important tasks of contemporary organic chemistry is the realization of reactions which supposedly do not work and their investigation. It is also necessary to pay attention to the investigation of all by-products of organic syntheses, because without this it will not be possible to determine the true mechanism of the processes under investigation.

A considerable amount of attention was paid at the conference to the analysis of kinetic characteristics and to the mechanism of complex homogeneous reactions. The classification of reactions according to the basic types (radical, molecule-radical, ionic, molecular-ionic, and molecular) was subjected to consideration. In this context the problem in regard to the competition between different mechanisms in actual chemical reactions was discussed. At the same time it was emphasized that molecular reactions are underestimated in contemporary organic chemistry and that the opinion prevails that radical reactions are always more advantageous than molecular reactions.

A discussion of the problem of ionic reactions was also launched. Organic chemists sometimes attach an extended meaning to the term ionic reactions and regard as ionic a considerable number of heterolytic reactions, for instance the reactions of electrophilic substitution in aromatic systems. However, these processes take place without formation of free ions. An interesting direction in the study of ionic reactions is the clarification of questions

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pertaining to the common nature of the mechanisms of ionic reactions in solutions and the mechanisms of electrochemical processes. The conference also noted that there is inadequate attention to inorganic reactions, although among them typical examples are encountered of the effect of structure on the reactivity of substances and also numerous examples of ionic mechanisms.

In many reports and statements made during the discussion the suggestion was advanced that experimental measurements in the field of the kinetics of chemical reactions should be expanded. At the same time, a considerable amount of interest was aroused by communications which dealt with mathematical methods for the solution of kinetic equations that give a macroscopic description to the kinetics of reactions under consideration. The desire was expressed that work on the mathematical theory of chemical kinetics be expanded and that the solution of systems of kinetic differential equations be carried out with more precision. Although the schedule of the conference was excessively heavy and highly diversified, it was noted in many reports and statements made at the conference that discussions of the problem of macrokinetics were lacking, i. e., insufficient attention was paid to relationships pertaining to the occurrence of chemical reactions under actual conditions complicated by the diffusion of the reacting substances and heat transfer. Another shortcoming in the organization of the conference was that no papers on chemical kinetics as applied to combustion were given. USSR science has to its credit great achievements in creating a theory of processes of combustion. However, at the present time the scope of work being carried out in this field is entirely insufficient. It is necessary to expand again the investigation of cold and hot flames and of processes of flame propagation and explosions.

The principal problem of chemical kinetics is that of directing processes or chemical transformation into the desired channels. It has not been shown adequately at the conference how this can be done on the basis of a detailed knowledge of reaction mechanisms. At the same time, the suggestion has been advanced that it ought to be possible to control chemical transformations once a sufficient knowledge of macroscopic stages of chemical reactions has been acquired. Macroscopic stages, which are composed of a number of elementary processes, lead either to the formation of relatively stable intermediate substances or the formation of final products of the reaction. As compared with the conventional way of conducting chemical reactions by establishing a set of conditions beforehand, i. e., at the very beginning of the reaction, action on the macroscopic stages which develop during the course of the reaction process is very effective.

Sometimes (particularly in the case of complex chain reactions) the initial period of the reaction plays a special role, so that the effects of different factors in the initial period and in a later period are not the same. In many reports presented at the conference, specific chemical processes (those of oxidation, polymerization, induced chlorination in complex organic systems, etc.) were discussed from the standpoint of the concept of macroscopic stages. Expansion of research on macroscopic stages of complex chemical processes is necessary.

The inadequate scope of the photochemical research that is carried out was noted at the conference. Although there is a lack of attention to this field, photochemistry is a powerful tool for the investigation of mechanisms of complex reactions. Very promising are investigations on processes of the phototransfer of electrons leading to the formation of ions and free radicals. A. N. Terenin's theory in regard to the induction of biradical states as a result of the action of light suggests that the role of biradicals in many processes of organic chemistry must be reviewed. Of great importance is the study of reactions which take place with an accumulation of energy in the reaction products. Such reactions may be regarded as models of the process of photosynthesis.

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In a number of statements made at the conference, the idea was stressed that a distinction which is too rigid is being made between homogeneous and heterogeneous processes. To counteract this tendency, one ought to investigate by every possible means the large group of [intermediate] homogeneous-heterogeneous processes.

An important place in the work of the conference was occupied by problems of catalytic activity and of the kinetics of heterogeneous catalytic reactions. Notwithstanding the immense practical importance of processes of heterogeneous catalysis and the great amount of scientific research which is being carried out in this field, the most important problems of the theory of catalysis have not yet been solved. Among these problems the cardinal one is that of the nature of catalytic activity. At the same time there is a pronounced tendency for mutual rapprochement between different points of view in regard to catalysis. The future theory of the selection of catalysts will presumably use the positive elements contained in present-day theories.

Many participants at the conference commented on the new theory of catalysis which assumes that there are free valencies on the surface of the catalyst and that heterogeneous chain reactions can take place. The principal postulates of this theory require direct experimental proofs. Although these postulates are completely plausible from the standpoint of logic, there are many facts which conflict with the theory. For instance, it has been noted that free atoms which are adsorbed on the surface lose their chemical activity. It is very important to obtain more information on the electrical state of the molecules adsorbed on the surface of the catalyst. It is necessary to take into consideration that ionic radicals may form on this surface in addition to free radicals. It is also necessary to continue work on the elucidation of the physical nature of the "free valency," particularly as far as metal catalysts are concerned. One must also establish the specific characteristics of the influence exerted by the structure of the molecules on the reactivity of these molecules in processes of heterogeneous catalysis.

M. M. Dubinin, Academician-Secretary of the Department of Chemical Sciences, Academy of Sciences USSR, stated in his address that the conference has given to scientists who work in the field of the theory of chemical processes an opportunity to meet again after long years, to renew former contacts, and to establish contacts with scientists who have become active in this field recently. Dubinin pointed out that there were nevertheless some drawbacks in the work of the conference: for instance, it has not been possible to organize a sufficiently broad discussion. The reason for this is evidently the fact that because of the short time which was available not all participants at the conference had the opportunity to study thoroughly enough the material published prior to the conference. Those who presented reports or participated in discussions held at the meeting limited themselves to reporting concrete scientific results and did not discuss general problems extensively.

Dubinin suggested that the Scientific Council on the Theory of Chemical Structure, Kinetics, and Reactivity and the Scientific Council on the Scientific Basis for the Selection of Catalysts at the Department of Chemical Sciences insure the organization of new conferences in the future and facilitate this organization. In considering the plans for scientific research work to be carried out by chemical institutions during 1956 and under the new 5-year plan, these councils must take into account the experience acquired at the present conference and reinforce their function as coordinating centers in connection with the development of work on the most important problems of theoretical chemistry.

It is essential that the collective creative work of chemical scientists of various specializations insure further success in the development of theoretical chemistry, which is an important branch of Soviet chemical science.

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